LECTURE-5

Water Pollution and Advanced Detection Techniques

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Water is an essential element of earth's natural environment. All living being depend on it, in one way or another. It is one of the most important sources for drinking, irrigation and industrial purposes. Growing urbanization, rapid industrialization without proper plan, excess use of chemical fertilizers, insecticides, pesticides in agriculture field has deteriorated the quality of water, causing water pollution. In broad perspective "Pollution" means such contamination of water or such alteration of the physical, chemical or biological properties of water or such discharge of any sewage or trade effluent or of any other liquid, gaseous or solid substance into water (whether directly or indirectly) as may, or is likely to, create a nuisance or render such water harmful or injurious to public health or safety, or to domestic, commercial, industrial, agricultural or other legitimate uses, or to the life and health of animals or plants or of aquatic organisms (Govt. of India, 1974). Pollution in water bodies can enter through one or more of the following ways:

i) Point Sources: Transfer of pollutants from municipal, industrial liquid waste disposal sites and from municipal and household hazardous waste and refuse disposal sites. The pollution from these sources can be measured directly or otherwise quantified and one can evaluated their impact directly.
ii) Non-point Sources or Diffuse Sources: Wash off and soil erosion from agricultural lands carrying material applied during agricultural use, mainly fertilizers, herbicides and pesticides. Runoff from urban streets, commercial activities, industrial sites and storage areas and there is no single outlet of such source but consists of a number of outlets.
iii) Change in the hydraulic regime of water system due to excessive water abstraction, construction of developmental works.

Broadly, the major sources of water pollution can be divided as urban and domestic waste, industrial waste, agricultural sources, mining wastes, induced contaminated source, radioactive substances etc. In municipal areas the solid waste is produced at a rate of 0.33 kg/capita/day and thus the production of solid waste by the urban population of the country is around 23 million tons per year. Therefore, urban and domestic wastes play a significant role in polluting the water. Industrial wastes discharge plays an important role in the deterioration of water quality specially in urban and industrial areas. Besides several environmental guidelines for industries in India, there is lack of facilities to treat the solid and liquid waste and the same is generally dumped in low lying/open area by these industrial units, which moves downwards to lower reaches causing pollution in ground water regime. To increase the yield, indiscriminate use of fertilizers has also resulted into higher concentration of some constituents like Nitrates and Phosphate. Pollution is therefore considered as a major threat at the system level involving environmental implications and needs to make efforts for its control and remediation.

Various pollutants present in water are measured through water quality parameters and can be broadly classified into following categories:

Physical parameters: appearance, temperature, turbidity, colour, taste, odour
Chemical parameters: all inorganic and organic substances (e.g. pH, acidity, alkalinity, hardness, conductivity, chlorides, sulphates, nitrates, nitrites, ammonia, fluoride, boron, heavy metals, pesticides, detergents, phenols, cyanide, radioactivity, oil and greese, organics, BOD, COD, DO etc.
Biological parameters: Total Coliform, MPN, Total plate count (TPC)

The water is being used as multipurpose resource in India. The main uses of water are public water supply, outdoor bathing & recreation, fisheries & wildlife propagation, irrigation & other agricultural uses, cooling in power plants, navigation and disposal of wastes. Most of these uses are often conflicting. In order for any water body to function adequately in satisfying any one of the above mentioned use, it must have corresponding degree of purity. In terms of quality, drinking water needs highest level of purity, whereas disposal of wastes can be done in any quality of water. Therefore there is great need to maintain the quality of water as it is as important as the quantity.

The Central Pollution Control Board has classified all water bodies including coastal waters in the country according to their "designated best uses" as given in the Table 1.

Table 1. Designated Best Use Classification of Surface Water (CPCB, 1978)

Designated Best Use	Quality Class	Primary Water Quality Criteria
Drinking water source without conventional treatment but with chlorination	A	Total coliform organisms (MPN/100 ml) shall be 50 or less pH between 6.5 and 8.5 Dissolved Oxygen 6 mg/L or more, and Biochemical Oxygen Demand 2 mg/L or less
Outdoor bathing (organized)	B	Total coliform organisms (MPN/100 ml) shall be 500 or less pH between 6.5 and 8.5 Dissolved Oxygen 5 mg/L or more, and Biochemical Oxygen Demand 3 mg/L or less
Drinking water source with conventional treatment	C	Total coliform organisms (MPN/100 ml) shall be 5000 or less pH between 6 and 9 Dissolved Oxygen 4 mg/L or more, and Biochemical Oxygen Demand 3 mg/L or less

Propagation of wildlife and fisheries	D	pH between 6.5 and 8.5 Dissolved Oxygen 4 mg/L or more, and Free ammonia (as N) 1.2 mg/L or less
Irrigation, industrial cooling and controlled disposal	E	pH between 6.0 and 8.5 Electrical conductivity less than 2250 micro mhos/cm, Sodium Absorption Ratio less than 26, and Boron less than 2 mg/L

LAKE POLLUTION

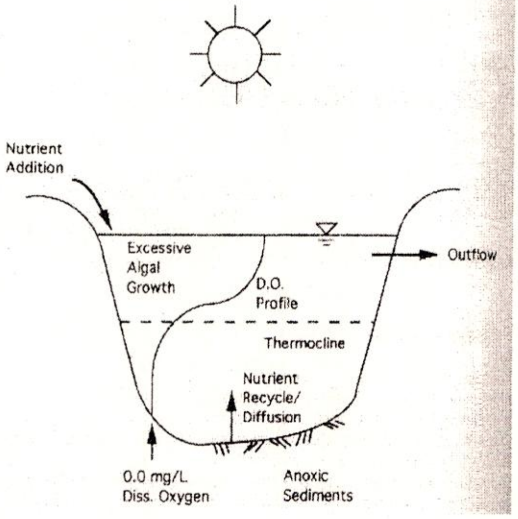
The chemicals such as nitrogen, phosphorous, carbon, sulfur, calcium, potassium, iron, manganese, boron, and cobalt which are essential for the growth of living thing, are called nutrients. Nutrients can be considered as pollutants when their concentrations are sufficient to allow excessive growth of aquatic plants, particularly algae. When nutrients stimulate the growth of alage, the attractiveness of the water body e.g. lake for recreational uses, as a drinking water supply and as a viable habitat for other living things can be adversely affected. Nutrient enrichment can lead to blooms of algae which eventually die and decompose. The decomposition of algae removes oxygen from the water, potentially leading to levels of DO that are insufficient to sustain normal life forms. Algae and decaying organic matter add colour, turbidity, ordours and objectionable tastes to water that are difficult to remove and that may greatly reduce its acceptability as a domestic water source. The process of nutrient enrichment, called Eutrophication, is an especially important process in the lake.

For the growth and reproduction, aquatic species require a number of nutrients but only carbon, nitrogen and phosphorous are the important nutrient. Plants require relatively large amounts of each of these three nutrients and unless all three are available, growth will be limited. The nutrient that is least available relative to the plant's needs is called the limiting nutrient. This suggests that algal growth can be controlled by identifying and reducing the supply of that particular nutrient. Carbon is usually available from a number of natural sources including alkalinity, dissolved carbon dioxide from the atmosphere, and decaying organic matter, so it is not often the limiting nutrient. Rather, it is usually either nitrogen or phosphorus that controls algal growth rates. In general, seawater is most often limited by nitrogen, while freshwater lakes are most often limited by phosphorus.

Major sources of both nitrogen and phosphorus include municipal wastewater discharges, runoff from animal feedlots, and chemical fertilizers. In addition, certain bacteria and blue-green algae can obtain nitrogen directly from the atmosphere. These life forms are usually abundant in lakes that have high rates of biological productivity, making the control of nitrogen in such lakes extremely difficult. Certain forms of acid rain can also contribute nitrogen to lakes. While there are several special sources of nitrogen, the only unusual source of phosphorus is from detergents. When phosphorus is the limiting nutrient in a lake that is experiencing an algal problem, it is especially important to limit the nearby use of phosphate in detergents.

Eutrophication refers to the excessive rate of addition nutrients, usually in reference to anthropogenic activities and the addition of phosphorous and nitrogen to natural waters. It is a natural process taking place over geologic time that is greatly accelerated by human activities e.g. due to soil erosion and biological production, lakes normally fill with sediments over thousands of years. As the lake fill up, the mean depth and detention time of the water body decreases. Sediments are in greater contact with overlying water, and nutrients recycle under anaerobic conditions via diffusion. With addition of anthropogenic nutrients, algae growth accelerated even further. Eventually a process that would have occurred over geologic time scales is accelerated to decades, and the lake becomes overly productive biologically causing some undesirable effects on water quality. The main problems of water quality are

- Excessive plant growth (green colour, decreased transparency, excessive weeds)
- Hypolimnetic loss of dissolved oxygen (anoxic conditions)
- Loss of species diversity (loss of fishery)
- Taste and odour problem



Lake Eutrophication and Nutrient recycle

The degree of eutrophication is a continuum and is called the trophic status of the water body. The trophic status may be categorized as

- Oligotrophic
- Mesotrophic
- Eutrophic

Eutrophic comes the Greek term meaning well-nourished. Oligotrophic systems are 'undernourished' i.e. biological production is limited by nutrient additions. Eutrophic systems are overfertilized by anthropogenic nutrient additions with concomitant water quality problems. Mesotrophic waters lie somewhere in between. The main factors controlling eutrophication are availability of sunlight for photosynthetic reactions and the concentration of nutrients required for growth.

Justus Liebig, in 1840 postulated an idea that growth of a plant is dependent on the amount of foodstuff that is presented to it in minimum quantity. This is known as Liebig's law of the minimum. According to this law, algal growth will be limited by the nutrient that is least available relative to its needs. Therefore the quickest way to control eutrophication would be to identify the limiting nutrient and reduce its concentration. Further, Liebig's law also implies that reductions in a nonlimiting nutrient will not provide effective control unless its concentration can be reduced to the point where it becomes the limiting nutrient.

TOXIC POLLUTANTS

Some of the pollutants are of serious concern and can not be neglected, are Heavy metals (zinc, copper, cadmium, lead, mercury, nickel, iron, manganese, arsenic, chromium) and Pesticides and Polynuclear Aromatics Hydrocarbons (PAH). Heavy metal pollution in its inorganic and organic forms is mainly caused by uncontrolled discharge of wastewaters of different types of industries. Leachates from landfill sites and mining waste dumps are other contributors of metal pollution. Organic pollutants (mostly organochloro and some persistent toxic substances in water bodies) got importance because of their carcinogenic character. They enter water bodies through point sources, non-point sources as well as through long range atmospheric transportation. The process of bio-accumulation and bio-magnification of these organic pollutants fresh water eco-system is of great importance.

HEAVY METALS

Metals are characterized by high thermal and electrical conductivity, high reflectivity and metallic luster, strength and ductility. From a biological perspective, however, it is more common to use broader definition that says a metal is an element that will give up one or more electrons to form a cation in an aqueous solution. With this definition, there are about 80 elements that can be called metals. The term heavy metal is less precisely defined. In chemical terms it can refer to metals with specific gravity greater than about 4 or 5, but more often, the term is simply used to denote metals that are toxic. The list of toxic metals includes aluminium, arsenic, beryllium, bismuth, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, nickel, selenium, strontium, thallium, tin, titanium and zinc. Some of these metals, such as chromium and iron, are essential nutrients in our diets, but in higher doses are extremely toxic.

In recent years, fluxes of the many metals from terrestrial and atmospheric sources to the aquatic environment have increased considerably. The metals can enter the aquatic environments through atmosphere and releases from point and non-point source. Point sources of metals include municipal sewage sludge and effluent outfalls to surface waters, direct releases to water courses from industrial units, and in some areas, acid mine drainage. Non-point sources of metals include natural weathering of geologic materials and anthropogenic sources such as runoff from manure and chemical fertilizers from farm fields and irrigation return flow. The sources for different metals in the environment include agriculture (As, Cu, Hg, Pb, Se and Zn), electrical power (As, Cd, Cu, Hg, Pb, Ni, Se and Zn), metallurgy (As, Cd, Cr, Cu, Hg, Pb, Ni and Zn), and wood and pulp processing (As, Cd, Cr, Cu, Hg and Pb). The elevated levels of Cu, Pb, Zn, and to a lesser degree Cd, can be due to corrosion within the urban water supply network

(Preuss and Kollmann, 1974). The use of detergents also creates a possible pollution hazard, since common household detergent products can affect the water quality. Angino et al. (1970) also reported presence of various elements, viz., Fe, Mn, Cr, Co, Zn, Sr and B in most detergents.

The elevated levels of trace metals in natural water systems pose a severe threat to the aquatic environment. Heavy metals are not biodegradable and enter the food chain through a number of pathways causing progressive toxicity due to the accumulation in human and animal organs during their life span on long term exposure to contaminated environments. Despite the presence of trace concentrations of Cr, Mn, Co, Cu and Zn in the aquatic environment, which is essential to a number of life processes, high concentrations of these metals become toxic. Therefore it is necessary to analyse the concentration of these metals in aqueous solution like water for water quality management. To estimate such metals in very very small quantities, advance technique and equipments are required. Atomic absoption spectroscopy has been proved itself to be most effective instrumental technique for quantitative determination of metals in liquid.

Some of the important metals found in ground water are discussed below with their sources of origin and their permissible limit prescribed by Bureau of Indian Standards and Word Health Organisation.

Iron (Fe): It is a known fact that iron in trace amounts is essential for nutrition. High concentrations of iron generally cause inky flavour, bitter and astringent taste to water. Well water containing soluble iron remain clear while pumped out, but exposure to air causes precipitation of iron due to oxidation, with a consequence of rusty colour and turbidity. The objection to iron in the distribution system is not due to health reason but to staining of laundry and plumbing fixtures and appearance. Taste and order problems may be caused by filamentous organism that prey on iron compounds (frenothrix, gallionella and leptothrix are called iron bacteria), originating another consumer's objection (red water). The presence of iron bacteria may clog well screens or develop in the distribution system, particularly when sulphate compounds in addition to iron may be subjected to chemical reduction. The Bureau of Indian Standards has recommended 300 μg/L as the desirable limit and 1000 μg/L as the maximum permissible limit for iron in drinking water (BIS, 1991). High concentration of iron may be attributed to the dissolution of iron bearing minerals from the soil strata.

Manganese (Mn): Manganese is an essential trace nutrient for plants and animals, which does not occur naturally as a metal but is found in various salts and minerals frequently in association with iron compounds. Manganese may gain entry into the body by inhalation, consumption of food and through drinking water. In general concentration of manganese in ground water is less than that of iron. A concentration of 100 μg/L has been recommended as a desirable limit and 300 μg/L as the permissible limit for drinking water (BIS, 1991). WHO has prescribed 0.5 mg/L as the provisional guideline value for drinking water (WHO, 1996). The presence of manganese above permissible limit of drinking water often imparts alien taste to water. It also has adverse effects on domestic uses and water supply structures.

Copper (Cu): The Bureau of Indian Standards has recommended 50 µg/L as the desirable limit and 1500 µg/L as the permissible limit in the absence of alternate source (BIS, 1991). Beyond 50 µg/L the water imparts astringent taste and cause discoloration and corrosion of pipes, fittings and utensils. World Health Organization has recommended 2000 µg/L as the provisional guideline value for drinking purpose (WHO, 1996). In general the principal sources of copper in water supplies are corrosion of brass and copper pipe and addition of copper salts during water treatment for algae control. Industrial sources can be listed for smelting and refining, copper wire mills, coal burning industries, electroplating, tanning, engraving, photography, insecticides, fungicides, coal burning industries, and iron and steel producing industries. The toxicity of copper to aquatic life is dependent on the alkalinity of the water. At lower alkalinity, copper is generally more toxic to aquatic life. Copper if present in excess amount in public water supplies enhances corrosion of aluminium and zinc utensils and fittings. High intake of copper may results in damage to liver.

Nickel (Ni): Nickel is extensively used in making stainless steel, Invar, Monel, Inconel, and all corrosion resistant alloys. It is also used in ceramic, special batteries, electronics, and space applications. Nickel in very small concentrations is found in earth's crust. Not commonly found in nature as a pure metal, it occurs in sulfides, arsenides, antimonides, oxides, and silicates. Nickel salts are soluble in water, as are many of its compounds. Certain nickel compounds have carcinogenic effects on animals, however, soluble compounds are not currently regarded as human or animal carcinogens. Nickel at trace level is essential to human nutrition and no systemic poisoning from nickel is known in this range. The level of nickel usually found in food and water is not considered a serious health hazard but excessive exposure with nickel salts like nickel subsulphides and nickel oxides can cause lung cancer and cancer of nasal sinus. World Health Organization has recommended 20 µg/L as the guideline value for drinking purposes (WHO, 1996). BIS (1991) has not prescribed the permissible limit for nickel in drinking water specifications.

Chromium (Cr): Found in the earth's crust, chromium is a naturally occurring metal in drinking water. The two important oxidation states of chromium in natural waters are +3 and +6. Chromium (+6) compounds are approximately 100 times more toxic than chromium (+3) salts. Inter-conversions of Cr(+3) and Cr(+6) occur in conditions similar to natural waters. Trivalent chromium may be nutritionally essential with a safe and relative innocuous level. Hexavalent chromium has a deleterious effect on the liver, kidney, and respiratory organs with hemorrhagic effects, dermatitis, and ulceration of the skin for chronic and subchronic exposure. Municipal wastewater release considerable amount of chromium into the environment. In the natural environment, Cr(+6) is likely to be reduced to Cr(+3), thereby reducing the toxic impact of chromium discharges. The pathways of chromium contribution to ground water are that the chromium containing industrial effluent from electroplating, leather tanning, cement industries, steel industries and photography discharged into stream, the hexavalent state chromium may be reduced to trivalent state and later adsorbed on the suspended particulate. In case, it could not be adsorbed, the chromium remain in the form of colloidal suspension, may precipitate and become part of stream sediment, from where it may reach to ground water through percolation containing shallow aquifers. A concentration of 50 µg/L has been recommended as a desirable limit for drinking water (BIS, 1991). WHO has also prescribed 50 µg/L as the guideline value for drinking water (WHO, 1996).

Lead (Pb): Lead is not considered an essential nutritional element and is a cumulative poison to humans. Acute lead poisoning is extremely rare. The typical symptoms of advanced lead poisoning are constipation, anemia, gastrointestinal disturbance, tenderness and gradual paralysis in muscles, specifically arms with possible cases of lethargy and moroseness. The major source of lead contamination is the combustion of fossil fuel. It is used to manufacture of acid accumulators, alkyl lead compounds for gasoline, tetraethyl lead as anti knock compounds, solders, pigments and paints, ammunition, cable sheathing, roofing material, piping material, including for drinking water, in manufacture of sulfuric acid, lead arsenate, insecticides, rubber etc. Lead is removed from the atmosphere by rain and falls back on the earth surface and seeps into the ground. Lead passes from the soil to water and to the plants and finally into the food chain. In drinking water it occurs primarily due to corrosion of lead pipes and solders, especially in areas of soft water. It may be noted that the use of soft water of slightly acidic pH and the use of lead pipes in service and domestic water lines may provide higher concentrations of lead at the consumers's tap, particularly when the water use is minimal in the household (overnight still water in pipes). The Bureau of Indian Standards has prescribed 50 µg/L lead as the desirable limit for drinking water (BIS, 1991). Beyond this limit, the water becomes toxic. WHO has also prescribed the same guideline value for drinking water (WHO, 1996).

Cadmium (Cd): Cadmium is found in low concentrations in rocks, coal, and petroleum, it is found in ground water more than in surface water as a natural occurrence. Therefore it may enter the water supply from variety of industrial applications including mining and smelting, electroplating, and pigment and plasticizer production, and leachates from landfills. Drinking water is generally contaminated with galvanized iron pipe and plated plumbing fittings of the water distribution system. USEPA has classified cadmium as a probable human carcinogen based on positive carcinogenicity testing. The Bureau of Indian Standards has prescribed 10 µg/L cadmium as the desirable limit for drinking water (BIS, 1991). Beyond this limit, the water becomes toxic. WHO has prescribed 3 µg/L cadmium as the guideline value for drinking water (WHO, 1996). The drinking water having more than 10 µg/L of cadmium can cause bronchitis, emphysema, anaemia and renal stone formation in animals. The effects of acute cadmium poisoning in humans are very serious, among them are high blood pressure, kidney damage and destruction of testicular tissue and red blood cells (Encyclopedia of Environmental Sciences, 1980). Even the low concentrations of cadmium are known to have detrimental effects on man, having been associated with hypertensive diseases. The international Agency for Research on Cancer classified cadmium among the chemicals which are probably carcinogenic to man (IARC, 1976). Therefore, an understanding of the conditions and mechanisms that regulate the mobilization and distribution of cadmium in the environment is essential.

Zinc (Zn): The presence of zinc can be detected only in traces in natural water. Zinc is an essential element for both animals and man and is necessary for the functioning of various enzyme systems, deficiency of which leads to growth retardation. Low intake of zinc results in retardation of growth, immaturity and anemia, condition known as 'zinc deficiency syndrome'. Symptoms of zinc toxicity in humans include vomiting, dehydration, electrolyte imbalance, abdominal pain, nausea lethargyness, dizziness and lack of muscular coordination. Zinc imparts undesirable, bitter astringent taste to water at levels above 5.0 mg/L (WHO, 1996). A higher concentration of zinc (>15 mg/L) is aesthetically objectionable in drinking water due to a milky appearance and a greasy film in boiling. The Bureau of Indian Standards has prescribed 5000 µg/L zinc as the desirable limit and 15000 µg/L as the permissible limit for drinking water (BIS, 1991). WHO has prescribed 3000 µg/L as the guideline value for drinking water (WHO, 1996). Zinc deficiency in human body may result in infantilism, impaired wound healing and several other diseases.

Arsenic (As): Ground water is expected to contain higher arsenic concentrations than surface water. Because of its presence in geological materials, arsenic can be traced in water as originated by natural processes or by industrial activities – industrial waste, arsenical pesticides and smelting operations. Generally, arsenic found in two state – As(+3) and As(+5) in ground water. As(+3) compounds are more toxic than As(+6) compounds. Arsenic compounds are skin and lung carcinogens in humans. The Bureau of Indian Standards has prescribed 50 µg/L arsenic as the permissible limit for drinking water (BIS, 1991). Beyond this limit, the water becomes toxic. WHO has prescribed 10 µg/L arsenic as the guideline value for drinking water (WHO, 1996).

Mercury (Hg): Mercury in natural waters can exist in three oxidation states: elemental mercury (0), the mercurous (+1) state and the mercuric (+2) state. The nature of the species and their distribution will depend upon the pH, redox potential, and nature and concentrations of anions which form stable complexes with mercury. In well-aerated water ($Eh \geq 0.5$ V) mercuric species will predominate whereas, under reducing conditions, elemental mercury should prevail. Presence of enough sulfide ion stabilizes bivalent mercury as hydrosulfide or sulfide complexes, even at very low redox potentials. Mercury forms a group of compounds called organic mercurials (e.g. Methylmercury). Mercurials have found widespread use in insecticides, fungicides, bactericides, pharmaceuticals and in manufactures of synthetic polymers. The principal target organ of inorganic mercury is the kidneys, with neurological and renal disturbances. Methyl mercury compounds are very toxic to the central nervous system; they are also the major source of environmental contamination. The Bureau of Indian Standards has prescribed 1 µg/L mercury as the permissible limit for drinking water (BIS, 1991). Beyond this limit, the water becomes toxic. WHO has prescribed 6 µg/L mercury as the guideline value for drinking water (WHO, 2005).

Sampling, Preservation and Processing

Non-breakable high density polyethylene plastic should be used for collection of samples for metal analysis. The containers should soaked in 10% nitric acid for 48 h and rinsed with deionized water several times prior to use. For dissolved metal analysis, water samples should be filtered through Whatmann 0.45µm pore diameter membrane filters. The filtered samples should then be preserved by acidifying with concentrated ultra pure nitric acid to pH<2 (5 mL concentrated HNO_3 per litre of sample) and stored at 4^0C in polyethylene bottles. For total metal analysis, 100 mL of unfiltered water samples should be acidified with 2 mL ultra pure nitric acid and digested on a hot plate till the volume reduced to around 30 mL. The digested samples should then be filtered and final volume should be made upto 100 mL with deionised water and stored at 4^oC for total metal analysis. The difference between the total and dissolved metal concentrations gives the concentration of particulate metal.

For volatile metal mercury, take 50 ml sample, add 5 ml conc. HNO_3, then add 10 ml 50% H_2SO_4 followed by 5 ml 6% $KMnO_4$. Keep this mixture at room temperature overnight. Reduce excess $KMnO_4$ by dropwise addition of 20% hydroxylammonium hydrochloride. Make up the content to 100 ml. Use the resultant for mercury estimation on AAS-VGA. For arsenic, take 100 ml sample, add 5 ml conc. HNO_3, then digest the sample on a water bath to reduce the volume 5 ml. Finally make up the volume 10 ml with 7 N HCl.

Techniques available for Metal Detection

- Atomic absorption spectroscopy
- Flame Emission
- Vapour Generation Accessory (VGA)
- Graphite Tube Atomizer (GTA)
- ICP Emission

Atomic absorption spectroscopy

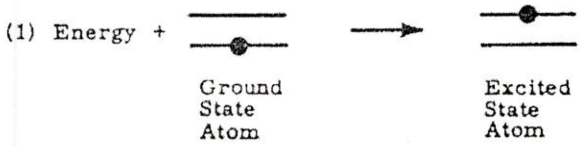
Atomic absorption spectroscopy is an absorption method where radiation is absorbed by non excited atoms in the vapour state. This technique involves the study of the absorption of radiation by neutral atoms in the gaseous state. In this technique, the sample is first converted into an atomic vapour and then the absorption of atomic vapour is measured at selected wavelength which is characteristic of each individual element.

Atomic Emission and Absorption

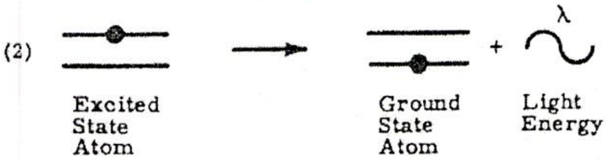
Every element has a specific number of electrons associated with its nucleus. The normal and most stable orbital configuration of an atom is known as the "ground state." If energy is applied to an atom, the energy will be absorbed and an outer electron will be promoted to a less stable configuration known as the "excited state." Since this state is unstable, the atom will immediately return to the "ground state," releasing light energy.

In atomic emission, the processes of excitation and decay are both involved. The sample is subjected to a high energy thermal environment in order to produce excited-state atoms. This environment can be provided by a flame or, more recently, a plasma. However, since the excited state is unstable, the atoms spontaneously return to the "ground state" and emit light. The emission spectrum of an element consists of a collection of emission wavelengths called emission lines because of the discrete nature of the emitted wavelengths. The intensity at an emission line will increase as the number of excited atoms of the element increases.

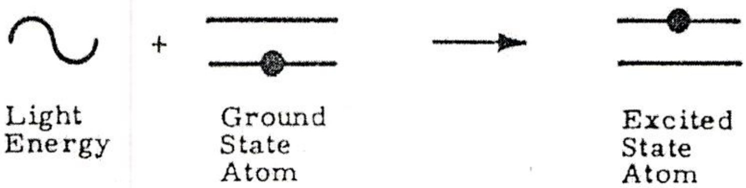
EXCITATION



DECAY



In the process of atomic absorption, the "ground state" atom absorbs light energy of a specific wavelength as it enters the "excited state." As the number of atoms in the light path increases, the amount of light absorbed also increases. By measuring the amount of light absorbed, a quantitative determination of the amount of analyte can be made. The use of special light sources and careful selection of wavelengths allow the specific determination of individual elements.



As we can see, there are some basic differences between atomic emission and atomic absorption. Using atomic emission, the flame serves a dual purpose. It converts the sample aerosol into an atomic vapor and then thermally elevates the atoms to an excited state. When these atoms return to the ground state, they emit light which is detected by the instrument. The intensity of light emitted is related to the concentration of the element of interest in solution. In atomic absorption, the only function of the flame is to convert the sample aerosol into atomic vapor which can then absorb light from the primary light source (hollow cathode lamp or electrodeless discharge lamp).

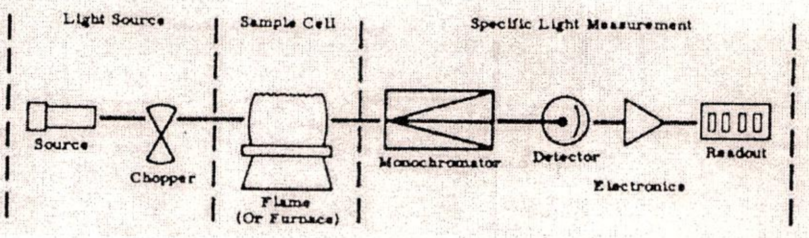
Atomic Absorption Instrumentation

There are five basic components of an atomic absorption instrument:

1. The light source which emits the spectrum of the element of interest
2. An "absorption cell" in which atoms of the sample are produced (flame, graphite furnace, MHS cell)
3. A monochromator for light dispersion
4. A detector which measures the light intensity and amplifies the signal

5. A display that shows the reading after it has been processed by the instrument electronics

A schematic diagram of atomic absorption instrument is shown below.



Working

The light source (hollow cathode lamp or electrodeless discharge lamp) emits a spectrum specific to the element of which it is made, which is focused through the sample cell into the monochromator. The light source must be electronically modulated or mechanically chopped to differentiate between the light from the source and the emission from the sample cell. The monochromator disperses the light, and the specific wavelength of light isolated passes to the detector, a photomultiplier tube. An electrical current is produced depending on the light intensity and processed by the instrument electronics. The electronics will measure the amount of light attenuation in the sample cell and convert those readings to the actual sample concentration.

Flame Emission Technique

This technique is generally used for such case where energy source (lamp) for that particular metal is not available. It provides better detection limits than that atomic absorption for Al, Ba, Li, K, Na and V. In this technique, optimum instrumental conditions will be the same as for absorption. The result will be better in emission if nitrous oxide-acetylene flame is used. The interferences will be the same as for the absorption technique.

Vapour Generation Accessory (VGA)

Some atoms As, Se, Sb, Sn vaporize when they come in contact of air-acetylene flame causing less atoms for absorption. Therefore, in order to have maximum concentration, they are converted into their respective hydride and atomized at lower temperature (upto 1000°C) using diffused flame.

Graphite Tube Atomizer (GTA)

In this technique, small liquid sample (5-25 µl) or solid (mg) are transferred directly to an electrically heated graphite tube or rod. The temperature programming is done. At low temp (~100°C) solvent is removed, at elevated temp (400-900°C) organic matter is destroyed by ashing and finally at high temp (2500-3000°C) residual material containing analyte is vaporized and atomized. Measure absorption at analyte wavelength.

ICP Emission

This technique is suitable for analysis of refractory elements U, B, P, Ta, Ti & W which are relatively insensitive to atomic absorption. Here, a chemically inert environment is created and to achieve very high temperature. Interferences present in atomic absorption is eliminated but spectral interferences are more common.

PESTICIDES

The term pesticide is used to cover a range of chemicals that kill organisms that humans consider undesirable and includes the more specific categories of insecticides, herbicides, rodenticides, and fungicides. However, the chemical pesticides are usually not target specific and therefore, may cause harm to non-target species and many of them are quite persistent for long periods in the environment. The indiscriminate application of pesticides provides the pollutional effect to a considerable extent. The pesticides join the water courses through the runoff from agricultural lands, industrial and urban effluents, spray operations for crop and disease vector control etc and may ultimately reach to the ground water through percolation. The pesticides may impart toxicity to the ground water and causes various health hazards. The unused pesticides and their degradation product and metabolites in the various compartments are known as Pesticide Residue.

Presently, synthetic organic pesticides are largely used to control insects and other pests. There are three main groups of synthetic organic insecticides:

i) Organo-Chlorine Pesicides: Also known as chlorinated hydrocarbons includes polychlorinated organic compounds mainly
   - Dichloro diphenyl trichloroethane (DDT) (o,p′-DDT, p,p′-DDT, p,p′-DDD, p,p′-DDE)
   - Diene group e.g. Benzene Hexa Chloride (BHC) isomers (α-BHC, β-BHC, γ-BHC & δ-BHC)
   - Endosulfan
   - Aldrin
   - Methoxychlor

ii) Organo-Phosphorous Pesticides: Phosphorous containing organic compounds e.g.
   - Ethion
   - Dimethoate,
   - Malathion
   - Methyl Parathion

iii) Carbamates: Nitrogen containing organic compounds used as insecticides (derivatives of carbamic acid) e.g. propoxur, carbaryl, and aldicarb

In addition, a number of herbicides, including the chlorophenoxy compounds 2,4,5-T (which contains the impurity dioxin, which is one of the most potent toxins known) and 2,4-D are common water pollutants.

One of the most well-known organochlorine pesticides was DDT (dichlorodiphenyltrichloroethane) which had been widely used to control insects that carry such diseases such as malaria, typhus, and plague. It was its impact on food chains, rather than human toxicity, that led to its ban even in India also. The main properties of organochlorine pesticides, that cause them to be particularly disruptive to food chains, are i) they are very persistent, which means they last a long time in the environment before being broken down into other substances, and ii) they are quite soluble in lipids, which means they easily accumulate in fatty tissue.

The organophosphates, such as parathion, malathion, diazinon, TEPP (tetraethyl prophosphate), and dimethoate, are effective against a wide range of insects and they are not persistent. However, the toxicity is much more than the organochlorines that they have replaced. They are rapidly absorbed through the skin, lungs, and gastrointestinal tract and, hence, unless proper precautions are taken, they are very hazardous to those who use them. Some of organo-chlorines are quite stable and persistent in aquatic medium while some of organo-phosphorous are significantly unstable in water and may degrade, hydrolyse or transform to other forms. The DDT metabolites are very stable.

Humans exposed to excessive amounts have shown a range of symptoms including tremor, confusion, slurred speech, muscle twitching, and convulsions. Acute human exposure to carbamates has led to a range of symptoms, such as nausea, vomiting, blurred vision, and in extreme cases, convulsions.

Presence of pesticides in ground water largely depends on their use in the adjoining and catchment area. The pesticides in water may be present in dissolved, precipitated (when present in excess) and suspended forms (when adsorbed on suspended particles). The solubility of pesticides in water besides their chemical structure (polarity) depends upon a number of factors e.g. pH, temperature, salt concentration, extent of agitation, organic matter (humic acid etc.), concentration of the medium and on partition between water and sediment phases and biotic activity.

Most of the organo-chlorine pesticides are non-polar in nature and have a tendency to dissolve in water to a very low extent and in general, the solubility of organo-chlorines in water range between 0.001 mg/L for DDT to 10.0 mg/L for γ-BHC (lindane). While the organo-phosphorous pesticides largely vary in their polar nature from almost non-polar to highly polar ones and subsequently, from sparingly soluble to highly soluble in water they are. In general the solubility range of organo-phosphorous pesticides may be from 24 mg/L for parathion to 25 g/L for dimethoate. However, all of them are soluble in most of the organic solvents making their handling easier.

Sampling and Preservation

For collection of sample for pesticide analysis, high quality dark glass container should preferably be used with teflon stopper. Polyethylene plastic container should not be used for collection of sample for pesticide analysis. Wash the container with acid, detergent, tap water, distilled water, acetone and finally with the working organic solvent. Store the samples at 4^0C.

Techniques available for Pesticide Detection

The detection of pesticide is done using the Chromatographic technique. This technique is based on the difference in the rate at which the components of a mixture move through a medium (called stationary phase) under the influence of some solvent or gas (called moving phase).

The following chromatographic methods are available depending upon mobile and stationary phase:

- Partition chromatography
- Adsorption chromatography
- Paper chromatography
- Thin layer chromatography
- Gas liquid chromatography
- Gas solid chromatography
- Gel chromatography
- Ion exchange chromatography

The analysis of pesticides residue in water is carried out on Gas Chromatograph using concept of Gas Chromatographic Separation. The separation of compounds is much better obtained by gas chromatography (GLC) and High Performance Liquid Chromatography (HPLC) technique. The quantification is ng to pg level.

Gas Liquid Chromatography (GLC) Technique

GLC based on Henry's law of Partition states

$$x/m = KC$$

Where x = mass of gas or vapour dissolved in liquid
m = mass of liquid on which x amount of gas dissolved
c = mass of gas or vapour dissolved in carrier gas
K = constant

The Gas Liquid Chromatography is based upon the partition between the gas and an immobile liquid phase.

Principle

In chromatographic process, a mobile phase passes over a stationary phase. When a sample containing some compound is place into the mobile phase, it will distribute between mobile and stationary phases. The speed with which the sample moves by the stationary phase is governed by its distribution ratio between the two phases. The greater the relative concentration of the sample in the mobile phase, the faster it will move. If a mixture of substance is introduced into the mobile phase, the rate of movement of the different components will be different if their partition coefficients between two phases are different.

The basic concept of GLC is derived from the partitioning of compounds between a gas (carrier) and a liquid (stationary phase). The liquid is either coated as fine film on the column wall or on an inert, finely divided support material in a column. To further complicate matters, the column is placed in an oven to vary the temperature. By varying the temperature it is possible to change the partition coefficients of the injected compounds, thus affecting the elution rates of the compounds and the separating capability of the column.

Instrumentation

The Gas Chromatograph is highly sophisticated instrument. The gas chromatographic separation is done in a tubular column made of glass, metal, teflon or fused silica. In this column a sorbent is filled/coated as the stationary phase. The mobile phase is a gas that flows continuously through the column. It is known as the carrier gas and serves to transport sample components in the column. The sample is introduced in the vapour form at the carrier gas entrance end of the column. The various components of the sample are sorbed on the stationary phase to different extents depending upon their partition coefficients. The carrier gas is the main driving force for the movement of samples through the column and the liquid provides the selective retarding force. The detector may be regarded as the brain of the chromatograph and the column as its heart.

The columns generally used in gas chromatography are Packed Columns, Open tubular columns and Support coated open tubular columns. Packed columns are prepared by packing metal or glass tubings with granular stationary phase, packing being prepared by coating the liquid phase over a size graded invert solid support. Open tubular columns are also referred as capillary or Gobay columns and are made of long capillary tubing (25-100 metres) having uniform and narrow internal diameter (0.025-0.075 cm). The inside wall of capillary tubing is coated with the liquid phase in the form of a thin (0.5-1 micron) and uniform film. The carrier gas flow faces least resistance because there is no packing in the column. Support coated open tubular columns are prepared by depositing a micron size porous layer of support material on the inside wall of a capillary column and then coating with a thin film of liquid phase. These columns have more sample capacity and an inlet splitter may not be required SCOT columns are preferred for trace analysis.

The choice of a detector will vary from application to application i.e. upon the criterion of Sensitivity needed, Compounds being analysed and availability. The following detectors are generally used:

- Electron capture detector (ECD): Specific and highly sensitive for halogenated compound.
- Flame ionization detector (FID): general for all organic compound except formic acid.
- Thermal conductivity detector (TCD): for all organic compound and permanent gases.

- Flame photometric detector (FPD): Highly sensitive for 'S' (394 nm) and 'P' (526 nm).
- Alkali flame ionization detector (AFID): very enhanced response for 'P'.
- Nitrogen phosphorous detector (NPD): An increase response to 'N' and high sensitivity to 'P'.

The water samples collected from the sampling sites can not be analysed directly on the instrument due to various reasons and need some processing before end-analysis. The aqueous phase is not acceptable to the instruments (GLC, HPLC), the compounds to be measured are extracted in some moisture free organic solvent. The concentration levels of pesticides in natural and drinking waters may be very low, therefore the dried organic solvent (extract) requires manifold concentration followed by proper clean up for removal of interfering co-extractives. Although the preprocessing methodology depends on the sample matrix, concentration and components to be analysed, however general steps of the processing are as follows:

- Extraction
- Drying
- Concentration
- Clean up
- End analysis

Extraction : The concentration of the pesticides residue in the water sample may be very low with complicated matrix which may interfere in the analysis of desired pesticides. Therefore it is necessary to separate out the desired pesticides from the bulk of water sample. A number of methods are available for extraction of pesticides from water on the quantitative basis but the cheapest and easiest is the Liquid-Liquid Extraction (LLE) method. The right selection of solvent must be made on the basis of knowledge regarding nature of pesticide(s) to be extracted and instrumental method adopted for end analysis. Methylene chloride, a polar solvent is ideal for extraction of many organo-chlorine and organo-phosphorous pesticides covering a wide range from less soluble to highly soluble pesticides in water.

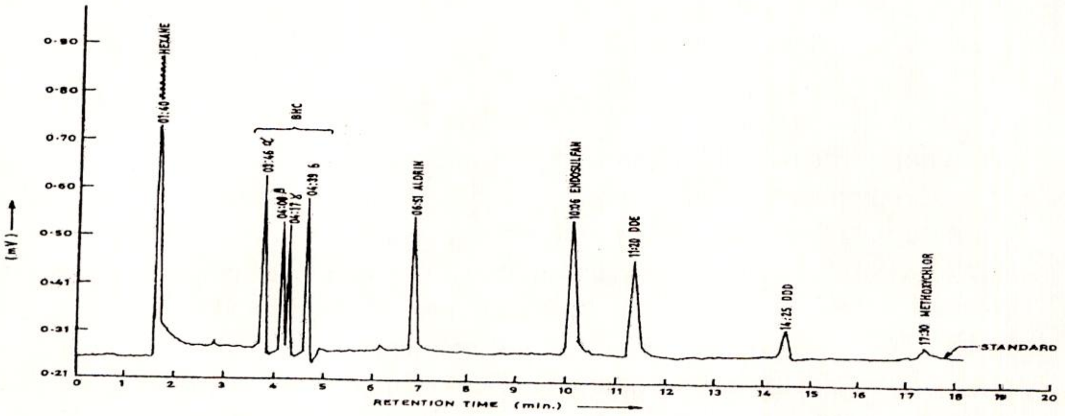
Drying : Drying of the extract is done by passing through anhydrous Na_2SO_4 column prepared by putting anhydrous Na_2SO_4 in a glass column with glass wool (Prewashed with acetone and solvent under use) pad in bottom to retain Na_2SO_4.

Concentration : The concentration is done in the Kuderna Denish evaporator. The dried extract is transferred to K. D. flask of the Kuderna Denish evaporator and evaporate the extract to 1-2 ml at the low temperature (40°C) under reduced pressure with the help of vacuum pump. The concentrated extract is transferred from evaporator flask to a 5 ml volumetric flask with small washings of the flask with selected solvent and make up the final volume upto the mark in 5 ml volumetric flask with selected solvent.

Clean up : Even using an efficient extraction method for removing organochlorine from the sample often yields matrix containing considerable amounts of co-extractives at the same time, which may interfere with the gas chromatographic analysis due to high sensitivity of the ECD for some compounds other than halogenated components. Hence identification and quantification are either inaccurate or impossible. Therefore, the extracts are cleaned up before end analysis. This is done either by liquid-solid column chromatography or acid wash. In column clean-up methods a suitable adsorbent (Florisil, alumina or silica gel) of very high purity and suitable mesh size is taken in a glass micro-column with solvent washed glass wool in bottom. In acid wash, the extract is washed with high purity H_2SO_4 and then the organic phase is separated.

End analysis : After processing the sample through these steps, the final concentrated and cleaned up sample is ready for instrumental analysis. Gas chromatograph is widely used and accepted instrument for quantification of pesticides residues at part per billion (ppb) and sub ppb levels.

Computation : If the detector response is linear in the working concentration range that is the peak height (area) versus concentration plot is linear, the concentration of a particular pesticide in unknown water sample can be computed by comparing peak height (areas) observed on the chromatograms for the standard and unknown sample.



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